Studies on Polymer Langmuir-Blodgett Films for Chemically Amplified Photoresists(高分子LB膜を用いた化学増幅型フォトレジストに関する研究)

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論文内容要旨

Chapter 1 Introduction

A general introduction about lithographic technology that is currently developed is briefly introduced. The semiconductors are manufactured by using diazonaphthoquinone(DNQ)-base photoresists and exposure tools equipped with mercury arc lamp illumination source. But to date, these modified materials have not met the requirements of high-volume manufacturing due to the inherent inefficiency of the photochemical process and the low quantum yield for the system. One way to increase efficiency is chemical amplification reaction in which a single photochemical reaction can result in a large number of subsequent reaction and an effective quantum yield. On the other hand, in the lithography process the thickness of the resist film becomes thinner, the need for more ordered and well-defined films has arisen.The attraction of the LB technique is the fact that it is possible to form a high ordered ultrathin film with which one can prepare the films desired more easily than spin coat film . The present work employs the principle of chemically amplified resists by utilizing polymer LB films to improve the performances of resists, such as increasing sensitivity, enhancement of resolution in the way of doped polymer LB films and hetero-deposited polymer LB films.

Chapter 2.Preparation of Photodegradable LB Films of Poly(*N*-dodecylacryl-amide-*co*-*tert*-butyl-4-vinylphenyl carbonate) and Application to Photopatterning

Copolymers [p(DDA-*t*BVPC)s] of *N*-dodecylacrylamide with *tert*-butyl-4-vinylphenyl carbonate were prepared to aim

at nano-fabrication of polymer LB films. The p(DDA-*t*BVPC)s could form stable condensed monolayers on the water surface and could be transferred successfully onto solid supports such as quartz, glass, and silicon wafer, giving Y-type polymer LB films. Deep UV irradiation on the polymer LB films induced a decomposition reaction of the polymer into the compound, which is soluble in alkaline solution. Subsequently, positive patterns and negative-tone patterns with high resolution were figured. The sensitivity increases with increasing mole faction of *t*BVPC and decreased with increasing the number of layers with the same content of *t*BVPC group. The p(DDA-*t*BVPC53) LB film deposited on the gold film or copper film performed a good resistance to wet etching. A fine etched gold or copper patterns with 1.0μm or 0.75μm was obtained by etching process. It was also demonstrated that the p(DDA-*t*BVPC53) LB film has a sufficient resistance to a dry etching process compared to PMMA cast film. The mechanism of degradation is that the side-chain cleavage of *t*-BOC group can only be induced forming phenol groups by deep UV irradiation by studying the change of FT-IR, UV-vis, and GPC spectra These photographic and etching characteristic properties of p(DDA-*t*BVPC)s LB films are expected to design the structure in molecular level and be used as a new type of positive photoresist.

Chapter 3 Preparation of Poly(*N*-alkylmethacrylamides-*co*-*tert*-butyl-4-vinylphenyl carbonate) LB Films and Application to Photopatterning

p(DDMA-*t*BVPC), p(TDMA-*t*BVPC), and p(iPMA-*t*BVPC) were prepared by using free radical copolymerization. The monolayer properties of copolymers on the water surface and their LB film formation were investigated by surface pressure-area isotherms and UV absorption spectra. All of them can form stable monolayers and can transferred onto solid substrates as a Y type of LB film.The structures of these copolymer are interesting; the copolymers can be decomposed through both main chain scission and side chain cleavage. Utilizing this special features we could fabricate fine positive-tone patterns with a resolution of 0.75 μm with p(iPMA-*t*BVPC39) LB film and a resolution of 1.0μm with p(DDMA-*t*BVPC60) and p(TDMA-*t*BVPC56) LB films. p(iPMA-*t*BVPC39) LB film is the more sensitive to deep UV from the result of sensitivity curves compared to p(DDMA-*t*BVPC60), and p(TDMA-*t*BVPC56) LB films. The etching property of the gold film was also investigated. The p(iPMA-*t*BVPC) LB films with 20 layers have a high etching resistance with a resolution of 1.0 μm. p(DDMA-*t*BVPC60) and p(TDMA-*t*BVPC56) LB films with 20 layers have also the sufficient resistance to wet etching giving a resolution of 1.5μm. From the results we expect that p(iPMA-*t*BVPC), p(DDMA-*t*BVPC), and p(TDMA-*t*BVPC) can be used in the lithographic process in future.

Chapter 4 Chemically Amplified Photoresists in Polymer LB Films

A preliminary study of the way to introduce TDBPIC into polymer LB films directly was carried out to aim at the development of chemical amplification system of p(DDA-*t*BVPC53) and p(iPMA-*t*BVPC39) LB films which have not been reported before.The sensitivity of these resist systems can be improved efficiently by using the polymer LB films. These systems can be processed in the positive mode, making it much more versatile than conventional method. A resolution of 1.0 μm was obtained in positive mode both of these resist systems. These results suggest that the catalytic reactions required to achieve high sensitivity in the LB film do not necessarily cause severe loss of resolution as being in spin-coat film. The etch resistance of these systems was also investigated. The results were sufficiently suitable for photomask fabrication. Both p(DDA-*t*BVCP53)/ TDBPIC LB film and p(iPMA-*t*BVPC39)/TDBPIC LB films can be clearly removed by organic solvent, such as chloroform, toluene, and ethanol. The efficiency of the photochemical reaction of these resist systems was quantitatively analyzed by using merocyanine dye as a probe of photogenerated acid. Although the samples were cast film, not LB films, it was found that the acid could be effectively amplified by the deep UV irradiation.

Chapter 5 Synthesis of Poly(*N*-neopentylmethacrylamide-*co*-9-anthrylmethylmethacrylate) and Application to Photoresists

The p(nPMA-AMMA10) was prepared by radical copolymerization. The copolymer can form a condensed monolayer on the water surface, which can transfer onto solid substrates such as quartz, glass, CaF_2, and silicon wafer, judging from the surface pressure-area isotherm and UV spectra. The positive-tone as well as negative-tone patterns could be printed on the silicon wafer by choosing the suitable irradiation light wavelength. The photolytic mechanism was investigated by using IR, GPC spectra and contact angle. Upon irradiation of these films with the light at ≤ 254 nm, main chain scission and/or decomposition of anthracene group took place, leading to the formation of low-molecular-weight compounds and carboxylic acid groups. On the other hand, the cross-linking reaction between anthracene groups occurred by the irradiation at 350nm, though it seems to be complicated. A resolution of 0.75 μm could be achieved in both positive-tone and negative-tone patterns of p(nPMA-AMMA10) LB films. Interestingly the copolymer LB films could be dissolved in alkaline aqueous after the irradiation at ≤ 254 nm. This suggests that the p(nPMA-AMMA10) LB films have a potential to act as a photoacid generator. The etch resistance of p(nPMA-AMMA10) LB film has sufficiently good to allow patterning of a gold and copper film with high resolution suitable for photomask fabrication.

Chapter 6 Photopatterning of Polymer LB Films with Hetero-deposited Layer Structure Based on Chemical Amplification

A new novel method of preparing chemically amplified resists was proposed by using two different LB films, aiming at achieving high sensitivity and high resolution. Two different LB films, p(nPMA-AMMA10) LB film, which acts as photogenerator layers, and p(DDA-*t*BVPC53) LB film was used to constructed hetero-deposited polymer LB film. It is the evidence that the well-oriented hetero-deposited polymer LB film could be formed from the UV absorption spectra.The patterns with a resolution of 0.75 μm by irradiating the hetero-deposited polymer LB film of 4 layers of p(nPMA-AMMA10) LB film and 40 layers of p(DDA-*t*BVPC53) LB film on a silicon wafer was obtained with deep UV irradiation followed by postexposure bake, finally developed with 1% TMAH aqueous solution. The sensitivity of the hetero-deposited polymer LB films strongly depends on the layer structure. This means that the sensitivity could be improved without loss of resolution in the polymer LB films by controlling the range of acid diffusion within the resist film and probably protecting from airborne contamination in chemically amplified resists using hetero-deposited polymer LB film.

Chapter 7 Photopattern Kinetics of Polymer LB Films Studied by Surface Plasmon Spectroscopy

The surface plasmon technique was utilized to understand the photopattern formation of the p(DDA-*t*BVPC53) LB films in detail. The minute change in the thickness could be precisely traced by the surface plasmon spectroscopy. The etching resistance of the polymer LB films was also investigated. It was found that p(DDA-*t*BVPC53) LB films with more than 14 layers (20 nm) has a high etching resistance against nitric acid solution.

Chapter 8 Summary

In this chapter, the main conclusion of this work were summarized.

審査結果の要旨

近年，光照射によって発生した酸分子の触媒反応を利用した化学増幅型フォトレジストが感度を飛躍的に増加させる方法の一つとして注目されている。本論文は、化学増幅型フォトレジスト能を有する高分子超薄膜を Langmuir-Blodgett（LB）法により作製し、新しい高分子材料及びフォトレジストへの応用について検討した研究の成果をまとめたものであり、全編 8 章より構成されている。

第 1 章は緒言であり、化学増幅型フォトレジストと LB 法について述べている。

第 2 章では、すぐれた LB 膜形成能を有する *N*-dodecylacrylamide（DDA）と光分解性を有する *tert*-butyl-4-vinylphenylcarbonate（*t*BVPC）の共重合体（p(DDA/tBVPC)s）を合成し、deep UV 光照射によるフォトパターニングについて検討している。deep UV 光の照射により *tert*-butoxycarbonyloxy（*t*-BOC）基の脱保護反応が起き、アルカリ水溶液の現像によりマスク限界の 0.75μm の解像度を有するポジ型フォトパターンが得られることを見いだしている。

第 3 章では、主鎖切断反応が可能な種々の *N*-alkylmethacrylamide と *t*BVPC の共重合体を合成し、そのフォトパターニングについて検討している。第 2 章と同様にポジ型のフォトパターンが得られ、側鎖切断反応が優先的に起こり、引き続き主鎖切断反応が起こることを明らかにしている。

第 4 章では、第 2 章、第 3 章で用いた共重合体と光酸発生剤の混合 LB 膜を作製し、化学増幅型のフォトパターニングの検討を行っている。共重合体のみの LB 膜に比べ高感度になるが、解像度は低下することを明らかにしている。

第 5 章では、アントラセンを有する高分子 LB 膜 p(nPMA/AMMA) のフォトパターニングについて検討を行っている。照射光の波長を適切に選択することによりポジ、ネガ両方のフォトパターンを描画することが可能であることを明らかにしている。

第 6 章では、p(DDA/*t*BVPC)と p(nPMA/AMMA)のヘテロ積層型 LB 膜のフォトパターニングについて検討している。アントラセンを有する共重合体が酸発生剤の働きをし、高解像度、高感度のポジ型パターンを与えることを見いだしている。さらに、ヘテロ積層の構造を制御することにより高感度化が可能であることを明らかにしている。

第 7 章では、表面プラズモン共鳴法による高分子 LB 膜のフォトパターン形成過程について検討している。高分子 LB 膜の耐エッチング性について検討したところ、p(DDA/*t*BVPC)LB 膜の場合、約 20nm でエッチング性を持つことを明らかにしている。

第 8 章は本論文の総括である。

以上要するに本論文は、化学増幅反応機構を LB 膜に導入しそのリソグラフィの性質を検討し、LB 膜の特徴を利用することで解像度と感度の向上を実現することを実証したもので、高分子化学及び材料化学の発展に寄与するところが少なくない。

よって、本論文は博士 (工学)の学位論文として合格と認める。